

Infrared spectroscopic imaging of complex samples

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Morphology-dependent infrared (IR) spectral response of materials is of contemporary practical need in the analysis of biological and synthetic materials. While significant work has recently been reported in understanding the spectra of thin films [1] and single particles with well-defined geometries (such as spherical [2] and cylindrical [3]), we report here on samples that consist of collections of particles with various packing density from sparse to dense. Within the framework of the T-matrix methodology [4], we theoretically model the importance of multiple scattering effects and computationally predict the impact of local particles' environment on the recorded IR spectra of monodisperse and polydisperse particles clusters with various degree of packing. Fourier-transform IR (FT-IR) spectra of clusters of electromagnetically coupled polymethyl methacrylate (PMMA) spheres with wavelength-scale diameters were recorded and compared to simulated results. Measured spectra agreed well with those predicted. Of note, when PMMA spheres occupy a volume greater than 18% of the focal volume, the recorded IR spectrum becomes almost independent of the cluster's morphological changes. This threshold, where absorbance starts to dominate the signal, matches the percolation threshold for hard spheres and quantifies the transition between the single particle and bulk behavior. Our finding enables an understanding of the spectral response of structured samples and points to appropriate models for recovering accurate chemical information from IR microspectroscopy data. The universality of this conclusion is of crucial importance for FT-IR microspectroscopy: one could simply neglect the morphology of the target if the target is packed densely enough, or for thicker samples.

References

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Preferred mode of presentation: Oral